

New aspects of the theory of ionic solvation and ion-ion interactions in solution

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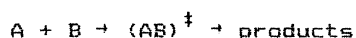
Abstract - The theory of the ferrous-ferric electron exchange in solution leads to new insights and new questions about both ion-ion interactions and ion-solvent interactions.

INTRODUCTION

Traditionally, the study of homogeneous electrolyte solutions is divided into the study of solvation, represented to some degree by Latimer's book (ref. 1), and the study of ion-ion interactions, represented by the Harned and Owen book (ref. 2). Up to the present time there seems to be a division of labor along these lines. But sometimes a problem comes up that deeply involves both branches of our field. Thus we find that in elucidating the ferrous-ferric electron exchange, a prototype oxidation-reduction reaction in solution, we encounter novel aspects of the solvent-mediated ion-ion interactions as well as novel aspects of the ion-solvent interactions.

IONIC STRENGTH EFFECTS

The classical theory for the effect of ions on a reaction rate constant is associated with the Livingston diagram (ref. 3,4) which relates to the rate constant k_{AB} for the reaction



of ionic species A and B in solution. Using the Debye-Hueckel approximation for single-ion activity coefficients as functions of molar ionic strength I gives a family of straight lines of the form

$$\ln[k_{AB}(I)/k_{AB}(0)] = -z_A z_B a_\gamma I^{1/2} \quad (1)$$

which make up the Livingston diagram. An extended Debye-Hueckel approximation gives a similar result with $I^{1/2}/[1+I^{1/2}]$ in place of $I^{1/2}$; the range of validity remains below $I=0.05M$.

Much more generally we may write the rate constant for an activation-controlled reaction as (ref. 5)

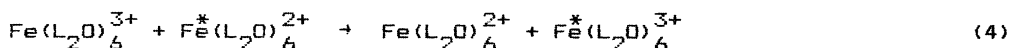
$$k_{AB} = \int g_{AB}(r) \hat{k}_{AB}(r) d^3r \quad (2)$$

where $g_{AB}(r)$ is the equilibrium pair correlation function (ref. 6,7) for the AB pair and $\hat{k}_{AB}(r)$ is the local rate constant, the rate constant when A and B are held at a separation r. In this formulation we have no single-ion activity coefficients; the effects of changing the ionic medium are all or nearly all in $g_{AB}(r)$. In the Debye-Hueckel approximation it is

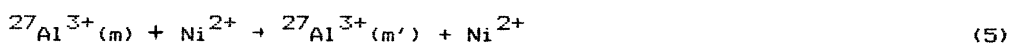
$$g_{AB}(r) \sim 1 - z_A z_B \lambda e^{-\kappa r} / r \quad (3)$$

where λ is the Bjerrum (or Landau) length and κ is the Debye shielding factor. More generally the pair correlation functions, which collectively provide a description of the equilibrium structure of a fluid that can be related to numerous measurable averages, can be calculated from models that specify the forces between the particles of the system (ref. 6,7).

We have been making a detailed study of the theory of the electron exchange reaction



where $\text{L}=\text{H}$ or D and $*$ denotes an isotopic label (Initially we take $\text{L}=\text{H}$.) It is interesting to compare the electron exchange rate with a certain NMR relaxation process written as a chemical reaction



where $\text{m} \rightarrow \text{m}'$ denotes a change in nuclear spin state of the $^{27}\text{Al}^{3+}$, because for both of these activation controlled processes the rate constant has the form

$$k_{23} = \int_0^\infty g_{23}(z) \hat{k}_{23}(r) 4\pi r^2 dr, \quad (6)$$

where $g_{23}(r)$ is the spatial pair correlation function for the $+2,+3$ species pair [either $\text{Fe}^{2+}, \text{Fe}^{3+}$ or $\text{Ni}^{2+}, \text{Al}^{3+}$] while $\hat{k}_{23}(r)$ is the local rate constant.

In the case of reaction (5), k_{23} is $1/T_1$ for the spin relaxation of $^{27}\text{Al}^{3+}$ while $\hat{k}_{23}(z)$ has the well-known Solomon-Bloembergen form (ref. 9,10). It is essentially a known function of r because it is controlled by the very fast electron spin relaxation rate in the aquonickel ion, which has been investigated independently (ref. 11). It is insensitive to the modulation of the spin-spin interaction by the diffusive motion of the ions (ref. 12). We assume that the hexaquo ions of given charge look sufficiently similar in solution so that $g_{23}(r)$ is the same for a ferrous-ferric pair as for an aluminum-nickel pair. Therefore we can "tune" g_{23} to fit the spin relaxation data and then use it in Eq. (6) for the electron transfer process (ref. 8).

We have calculated the ion-ion pair correlation functions in the solutions relevant to the study of the electron transfer reaction by beginning with McMillan-Mayer level models (ref. 8,13,14), i.e. models for the solvent-averaged force between the ions. It is often said that such models replace the molecular solvent by a continuum, but this need not be the case: In McMillan-Mayer theory the solvent is treated as a molecular fluid that is projected out of the equations for the ion-ion pair correlation functions under the conditions corresponding to osmotic equilibrium (ref. 14). On the other hand the assumption that three-body and higher solvent-averaged solute-solute potentials can safely be neglected has not been adequately tested. The ion-ion pair correlation functions were calculated from the models by the HNC approximation (ref. 6,7). It is interesting to notice that the picture emerging from the first calculations of MM ion-ion pair potentials from BO-level models (ref. 15,16) is that the resulting pair potentials show more effect of the structure of the solvent than our Gurney type models which have

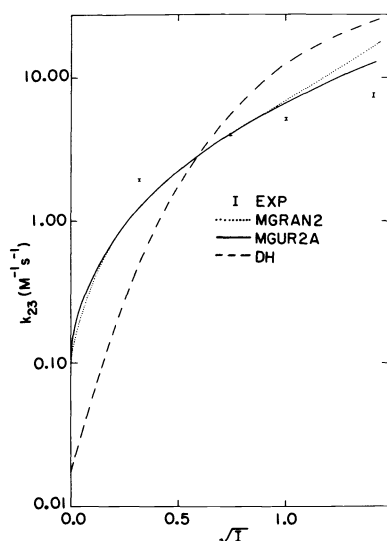


Fig. 1. k_{23} as a function of $I^{1/2}$

DH is an extended Debye-Hueckel approximation.

... granular model

— Gurney model

[From ref. 8 where details may be found.]

been adjusted to fit various solution properties (ref. 8). However our granular models, which are intermediate with respect to manifestations of the structure of the solvent, give rate constants that agree with those from Gurney models in the present study (ref. 8).

The local rate constant in the electron exchange process can be calculated by adapting the theory established by R. A. Marcus. (ref. 8,17) A crucial new ingredient is the large-scale quantum calculation of the interaction of the initial and final states in the electron transfer process. (ref. 18,19)

It was found for *both* electron transfer and spin relaxation that, if the minimum separation of the hexaaquo ions was 6.9Å, where the spherical envelopes of the hexaaquo complexes touch, then the calculated rate constant was far smaller than the experimental. However the closest approach of two hexaaquo ions is obtained in a *shoulder in armpit* configuration, in which the octahedral complexes approach on a common D_{3h} axis in a staggered orientation so the lobes on one aquo complex fit into grooves on the other. Then it is estimated that the separation can be as small as 4.6Å; the rates calculated on this basis agree with experiment. (ref. 8) This remarkable result has been confirmed by the neutron diffraction studies of Enderby and coworkers who find that in $4\text{mNiCl}_2(\text{aq})$ there are many pairs of hexaaquo nickel ions with center-to-center distance as small as 4.6Å (ref. 20). [Of course it is necessary to construct the solvent-averaged pair potentials in the model calculations of $g_{23}(r)$ so they are consistent with this small closest center-to-center distance and with limited orientational freedom when r is less than 6.9Å]

Another test of the adequacy of these calculations is the comparison of calculated and experimental ionic strength dependences of the rate constant for the electron transfer reaction; the feature we set out to study. Fig. 1 shows a significant improvement over the ionic-strength dependence calculated by means of extended Debye-Hueckel theory. There is some support for an explanation of this improvement in terms of a tendency to form ion pairs (most likely between Fe^{3+} and ClO_4^-), which is captured by the HNC approximation (ref. 21). Then the rate constant may be expected to depend on the specific composition of the electrolyte rather than solely on the ionic strength. Specific effects are indeed observed (ref. 21,22).

SOLVENT ISOTOPE EFFECTS OF IONIC SOLVATION

Now we turn to the investigation of the solvent isotope effect on the ferrous-ferric electron transfer, which is 2-fold slower in D_2O than in H_2O (ref. 23,24). (cf. Eq. 4) The seat of this effect is surely not in the g_{23} factor in Eq. (6). Can one expect that the k_{23} is sufficiently sensitive to whether $L=D$ or $L=H$ to account for the solvent isotope effect on k_{23} ?

We know from the outset that the change of solvent from H_2O to D_2O has significant thermodynamic consequences for metal hydration complexes (ref. 25-27). The solvent-isotope effect on thermodynamics is mainly due to changes in vibrational frequencies in the hydration complexes when H is changed to D, while it turns out to be the corresponding changes in distances that give the kinetic effect in reaction (4). Even so, the free energy effects for +1 and +2 ions are so small, in the sense we next describe, that one may doubt that there can be a measurable kinetic isotope effect for an outer-sphere electron transfer mechanism. Thus we consider the process



for which we define $\Delta G^\circ \equiv G_z$, $\Delta S^\circ \equiv S_z$, and $\Delta H^\circ \equiv H_z$. The data for $H_2O \rightarrow D_2O$ transfers for many electrolytes are characterized by extensive *entropy-enthalpy compensation* (ref. 25). It may be recalled that, for a series of similar processes in which one of the reactants Y is varied at a given temperature T, the equation

$$\Delta H(T, Y) = \Delta H^*(T) + T^*(T) \Delta S(T, Y) \quad (8)$$

is a statement of the Barclay-Butler rule. Here ΔH^* and T^* are coefficients which do not depend on Y although they do depend on T. The experimental and theoretical basis for this rule in solvation processes has been discussed by H.S. Frank (ref. 28). Lumry's law (ref. 29) states a stronger condition, namely $T^*(T) \cong T$ for processes in aqueous solution near room temperature if they are dominated by effects in the solvent in the neighborhood of the solute particles.

For Eq. (7) in the case of many $z=+1$ and $z=2$ ions, all at $T=298K$, it is found that the Barclay-Butler rule applies with $\Delta H^* \sim 0$ and $T^* = 298$, an exceptionally simple and striking example of Lumry's law (Fig. 24 of ref. 25). The requirement that this enthalpy-entropy correlation be maintained consistently for ions of charge +2, +1, and -1 yields relatively small values for G_z/RT : Li^+ , -0.07; Na^+ , 0.07; K^+ , 0.18; Mg^{2+} , 0.23; Ca^{2+} , 0.13; Ba^{2+} , 0.34. Over this range of ions H_z/RT varies over a unit (ref. 25). It is a challenge to find the molecular significance of this compensation effect.

Accordingly, Newton and Friedman calculated the O-L stretch and the libration frequencies of water molecules in ion-hydrate complexes by an *ab initio* application of Schrodinger's equation to ion-hydrate clusters (ref. 26, 27). Previous *ab initio* studies of $M(H_2O)_n^{z+}$ clusters, with M^{z+} either a metal ion or a point charge, and $n=1$ or 3, indicated that the O-H bond strength was appreciably sensitive to the ionic charge. We studied larger ionic clusters with $n=8$, and with M^{z+} either Na^+ , Mg^{2+} , or Al^{3+} . In each $n=6$ case the total cluster energy was minimized, subject to the constraint of T_h symmetry (octahedral MO_6 framework). The resulting frequencies and distances are given in Figs. 2 and 3.

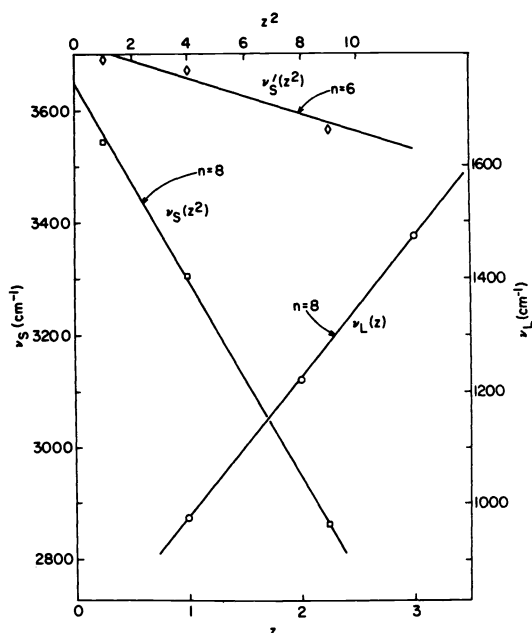


Fig. 2 Effect of ion of charge z on frequency ν_S for OH stretch and ν_L for libration. From ref. 26.

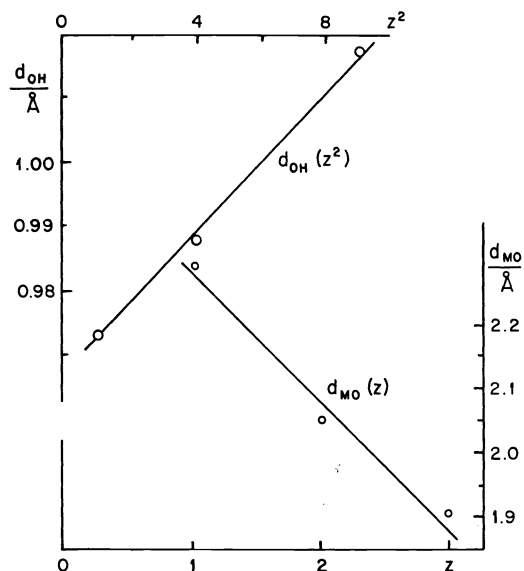


Fig. 3. As in Fig. 2 but showing variation of OH and MO distances. From ref. 27.

The remarkable difference in charge-dependence of ν_L and ν_S (Fig. 2) is the clue for resolving the puzzle in the G_z data. A qualitative interpretation is that ν_L increases with increasing z because of the enhancement of hydrogen bonding to second-shell water as well as the increased charge-dipole interaction with the metal ion. The O-H stretch frequency ν_S , in contrast to ν_L , decreases because of the effect of Coulombic interaction of M^{z+} with the O and H atoms of the inner shell water, giving a smaller MO distance and longer, and hence weaker, OH bonds. The non-linear dependence on z is striking.

The calculated ν_L values are somewhat larger than those observed in various salt hydrate crystals (ref. 27). For example, the cesium alums exhibit ν_L in the range from 500 to 1000 cm^{-1} , with the larger values presumed to characterize water in the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex, while ν_L from 534 to 836 cm^{-1} has been assigned to water in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For this and other reasons we shall scale ν_L by a factor of 0.7 as described below (ref. 26).

To calculate the solvent isotope effect (free energies of transfer) in terms of the frequencies of the water modes, assuming that they contribute additively, we may write

$$G_z/RT = -\sum_j f_j (\nu_j - \nu_j^0) \quad (9)$$

where ν_j is the frequency of the j^{th} intermolecular or intramolecular mode of the water in the hydration shell, ν_j^0 is the corresponding frequency in bulk water, and f_j is the zero-point energy factor

$$f_j = \frac{1}{2} [1 - (\mu_{j\text{H}}/\mu_{j\text{D}})^{\frac{1}{2}}] \quad (10)$$

where $\mu_{j\text{L}}$ is the reduced mass of the j^{th} mode.

For the present purpose we retain each mode that satisfies two conditions; its frequency is significantly z -dependent and it involves primarily L-atom motion, i.e. $\mu_D/\mu_H \approx 2$. Thus we are left with the stretch ν_S and libration ν_L modes. Employing the information displayed in Fig. 2 we obtain (ref. 26)

$$G_2/RT = B_0 + 18zB_L + 12z^2B_S \quad (11)$$

where $B_L = (f_L/RT)dv_L/dz$, $B_S = (f_S/RT)dv_S/d(z^2)$, and where $B_0 = G_0/RT$ is taken as an adjustable parameter; G_0 is formally the transfer free energy for a discharged ion. ($G_0/RT = -0.083$ for Ar)

In this way we find, using the unscaled ν_L ,

$$G_2/RT = 2.26 - 2.96z + 0.696z^2 \quad (12)$$

where G_0 has been adjusted to make $G_1 = 0$ in view of the thermodynamic data for the transfer reaction. Then we find $G_2/RT = -0.88$ and $G_3/RT = -0.36$, in poor agreement with the data. However the qualitative aspect, the possibility of substantial cancellation of the z and z^2 terms for 1+ and 2+ ions, is promising.

If we redetermine the coefficients B_0 and B_L in Eq. (11) by a least squares fit (with the given B_S) to the data (ref. 26), then we have, in place of Eq. (12),

$$G_2/RT = 1.13 - 1.83z + 0.696z^2 \quad (13)$$

giving $G_1/RT = 0.0$, $G_2/RT = 0.25$, $G_3/RT = 1.90$, and $(G_3 - G_2)/RT = 1.65$, in good agreement with the thermodynamic data. The -1.83 coefficient of z implies a scaling of ν_L ; a 30% reduction, which brings the calculated librational frequency for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ just within the upper range of crystal hydrate data. We may conclude that the (state-dependent) librational modes are critically important to the solvent isotope thermodynamics.

While the calculations in ref. 26 give results that are reasonably close to the Hartree-Fock limit, there must be some question, as to whether similar results would be obtained if the calculations could be made for hydration clusters with many (say 50 or more) water molecules in the neighborhood of each ion. A further question concerns the changes which would be found if electron correlation were incorporated in the calculations. Moreover, to complete the analysis of the thermodynamic data using model calculations, we need dv_L/dT and dv_S/dT , both as functions of z . These coefficients cannot be obtained by the methods used in ref. 26. These temperature derivatives are not well known even in real water. The important effect is expected to be strong dependence of ν_L on temperature since the Lumry's law behavior requires temperature-dependent thermodynamics different from what one derives for a simple harmonic oscillator with temperature-independent force constant. The librational modes are the leading candidates for temperature dependent force constants; for them the effective potential is entirely due to intermolecular interactions and therefore is temperature-dependent. All of these considerations invite the study of relevant models, having one ion and many water molecules, by molecular dynamics simulation, with the incorporation of path integral techniques to accommodate the nuclear quantum effects and, conceivably, the configuration interaction contributions to the electronic quantum effects.

SOLVENT ISOTOPE EFFECT ON RATE CONSTANT

We denote by k_H (k_D) the rate constant in Eq. (6) for reaction (3) when $L=H$ ($L=D$). The relevant theory, a modest extension beyond what was already available (ref. 30) is given in ref. 27, where it also is applied to evaluate k_H/k_D with the help of the data in Fig. 3. The H \rightarrow D shift in vibrational frequency, which is the dominant factor in the *thermodynamic* isotope effects considered above, is not so important for the *kinetic* isotope effect k_H/k_D . The dominant factors here are the shifts in geometry between the H and D systems; these shifts enter the rate constant through the Franck-Condon factors. Accordingly, in the calculations, we can safely employ mean frequencies, averaged with respect to $z=2$ and $z=3$.

The results are shown in Table 1 in terms of multiplicative contributions to k_H/k_D from the various modes of motion of the six water molecules in the hydration complex of a ferrous (2) or ferric (3) ion. Taken together these results give a factor in the range from 1.8 to 2.1, which is satisfactory agreement with the experimental data. The uncertainty in the librational contribution could be reduced in a calculation with many more water molecules of the sort mentioned above.

TABLE 1. Contribution of Various Modes to k_H/k_D .

Class	M=	1	2	3
Description of local mode		M-O stretch	O-H stretch	Libration ^(a)
g_M ^(b)		12	24	36
μ_M^H /dalton		18	0.948	0.550
μ_M^D /dalton		20	1.79	0.930
$\nu_M^{(2)}$ /cm ⁻¹		390	3484	853
$\nu_M^{(3)}$ /cm ⁻¹		490	3016	1033
$d_M^{(2)}$ /pm		212 ^(c)	99 ^(c)	7 (10)
$d_M^{(3)}$ /pm		198 ^(c)	102 ^(c)	0
k_H/k_D		1.11	1.43	1.14 (1.31)

(aa) Adapted from ref. 27.

(a) As in ref. 26 the effect of librational motion was investigated by considering the wagging mode.

(b) Number of local modes in class.

(c) O-L distance. See ref. 26.

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